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TITLE : A CATALYTIC APPROACH FOR THE DEVELOPMENT OF NEW METHODS IN ORGANIC SYNTHESIS

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A Catalytic Approach for the Development of New Methods in Organic Synthesis

A Short Resume of the Plan Proposed for Investigation

SUBMITTED TO

SWAMI RAMANAND TEERTH MARATHAWADA UNIVERSITY, NANDED

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SCIENCE

BY

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A Catalytic Approach for the Development of New Methods in Organic Synthesis

1. Introduction

Organic synthesis has a long history that can be traced back to ancient times. The ultimate goal of organic synthesis is to assemble a given organic compound from readily available starting materials and reagents in the most efficient way. The term "catalysis" was first employed by Berzelius in 1836 to identify a entity capable of promoting the occurrence of a chemical reaction by a "catalytic contact".

Catalysis is an amazing phenomenon in which the rate of chemical reaction is changed due to the participation of a substance, termed as catalyst, without being consumed by the reaction itself. Catalysis represents an important field of chemistry and chemical industry. Catalysis is involved in the production of most industrially important chemicals. The most important biochemical processes also involve catalysis. In applied science, catalysis research is a key area which involves many areas of chemistry, especially organometallic chemistry and material science. Catalysis is related to many aspects of environmental science. Due to the generation of reduced amount of waste, the catalytic reactions are preferred in eco-friendly green chemistry which opposes the stoichiometric reactions that involves the consumption of all reactants thereby forming more side products. The catalysis has attracted much attention in organic synthesis as it often affords access to unique reactivity and selectivity under mild conditions.

A catalyst provides an alternative reaction pathway to the reaction product. If this alternative pathway has lower activation energy than the reaction pathway without catalyst, then the rate of the reaction increases. Proton (H^+) is the most common catalyst. Number of transition metals and transition metal complexes are also used as catalysts in catalysis. Nowadays an important target in the organic chemistry is the development of new catalysts and reagents which are more active and selective than the traditional ones, which are easy to handle, often reusable and are very important from environmental point of view.

In organic synthesis there are various kind of catalysts are practiced, which works either heterogeneous or homogeneous manner for the development of methods. However, there are number of catalysts/reagents/techniques such as Organocatalysts,

Polymer Supported Reagents, Phase Transfer Catalysts, Microwave Irradiation/Activation used for the development of new methods in organic.

2. Review of Literature and Development in the subject

(Previous work done in the relevant area):

The present work with our research group involves the development of new methods in various organic transformations using various cartalysts:

1. An Efficient Synthesis of Bis(Indolyl) Methanes Using Phenyl Phosphonic Acid. [1]
2. Reduction of Carboxylic Acids to Alcohols Using Cyanuric Chloride and Borohydride Exchange Resin.[2]
3. Multicomponent Biginelli, Synthesis of 3,4-Dihydropyrimidin-2(1H)-Ones Catalyzed by Phenyl Phosphonic Acid.[3]
4. Microwave Assisted Synthesis Of Triaryl Phosphorothionates.[4]
5. An Efficient Method for the Synthesis of Bis (Indolyl) Methanes Using Phosphonitrilic Chloride Trimer.[5]
6. A Mild and Efficient Method for the Synthesis Of Acyl Azides From Carboxylic Acids Utilizing Phosphonitrilic Chloride.[6]
7. Synthesis of methylene dioximes using PEG–400 as a phase transfer catalyst under microwave irradiation.[7]
8. Beckmann Rearrangement of Ketoximes to Amides Using Phenyl Phosphonic Acid.[8]
9. Reduction of carboxylic acids to alcohols using phosphonitrilic chloride and sodium borohydride Pelagia.[9]
10. Synthesis of Aryl Esters by Activation of Carboxylic Acids Using Phosphonitrilic Chloride.[10]
11. Synthesis Of *p*-Nitrobenzoates of Phenols by Activating *p*- Nitrobenzoic Acid Using Phosphonitrilic Chloride.[11]
12. Reductive Amination of Carbonyl Compounds Using Lignin Sulphonic Acid and Sodium Borohydride.[12]

3. Objectives of Research/ Proposed Hypothesis:

The creativity and art of organic synthesis has reached an interesting stage in its development. Although we have some excellent methods to effect the construction of target molecules with ever increasing level of complexity, there is need to find new, strategically important processes which are environmentally cleaner, more efficient and which lead to greater structural variation in a shorter period of time.

The objectives of the proposed research project are as:

1. To design effective catalysts for various organic transformations.
2. To enrich chemistry with another useful strategy for catalysis.
3. Extending the research for catalyst to new domain targeting the various organic transformations.
4. To develop highly chemoselective method.
5. To tolerate variety of functional groups.
6. The method for the transformation will be operationally simple to perform with easy work up procedure and reduce reaction time.

4. Methodology to be adopted:

The proposed work will lead to the application of new catalysts for the development of new methods in organic synthesis in order to increase the rate of reactions, product yields, product purity, environmental friendly etc.

1. Literature survey
2. Development of new methods using new catalysts.
3. Use of microwave irradiation technique to organic reactions.
4. The synthesized compounds will be crystallized from proper solvents and purity of products will be monitored by TLC.
5. The product will be purified by column chromatography.
6. The structure of the synthesized compounds will be confirmed by IR, NMR, ^{13}C NMR and Mass spectral data.

5. Importance of study/ Society application:

Organic synthesis has seen enormous growth in the development of new reagents, catalysts, strategies, transformations and technologies often involving the concepts of atom economy and selectivity which lead to the development of new methodologies in the recent years.

- **International status**

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   Rajasthan

- **Significance of the study**

Considering that most of the organic chemical reactions require catalyst, the research of catalysis acquire ever greater interest and significance. Catalysts, in the definition by Berzelius and others in the 19th century, are materials which change the rate of attaining a chemical equilibrium without themselves being changed or consumed in the process. Some catalysts achieve amazing activities, so that very small quantities of catalyst can convert thousands or millions of times their own weight of chemicals. Equally significant is the selectivity; usually thought of in terms of a catalyst accelerating one of a number of competing reactions, but also possible by virtue of a catalyst selecting one reagent out of a complex mixture.

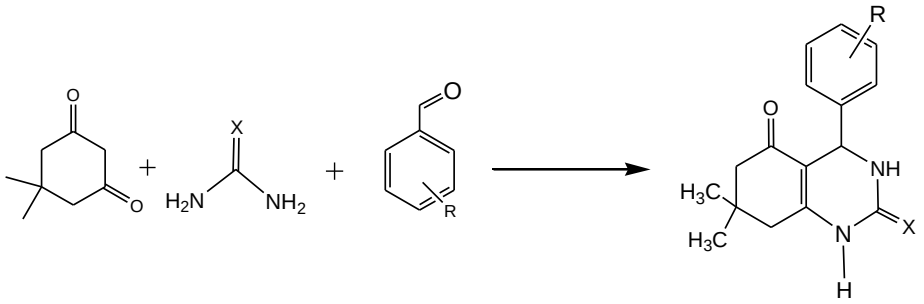
6. Proposed work Plan/ Formulation and Structure of Study:

Catalysts are needed to facilitate chemical reactions so that they occur at useful rates and with preference to the desired product. The catalysts that make the reaction go fast ; make the reaction go to the desired products ; and last a long time or regenerate themselves allows us to carry out chemical reactions in the most efficient, economical and environmentally responsible manner.

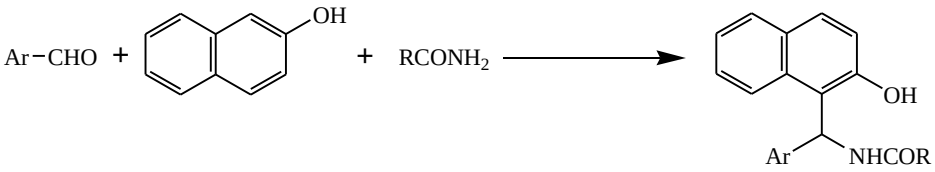
1. In view of the above discussion, Catalysts will be designed and utilized for the development of new methods in organic synthesis.
2. The success of the catalysts for the reaction will be confirmed by IR, NMR, Mass and ^{13}C NMR spectral data of the products.

In the present work, we plan to design and utilize the catalysts for the development of methods in organic synthesis. The following organic reactions will be carried out:

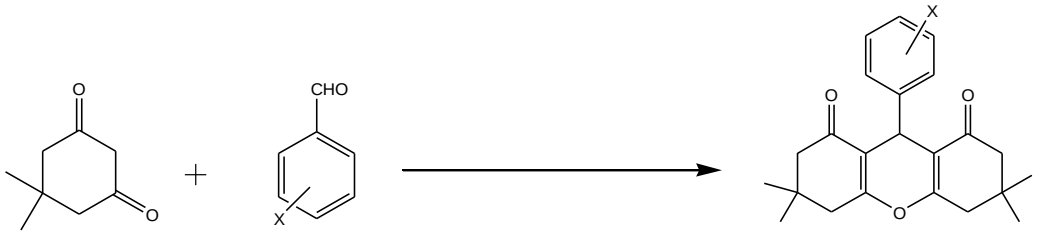
1. Synthesis of Octahydroquinazolinone.



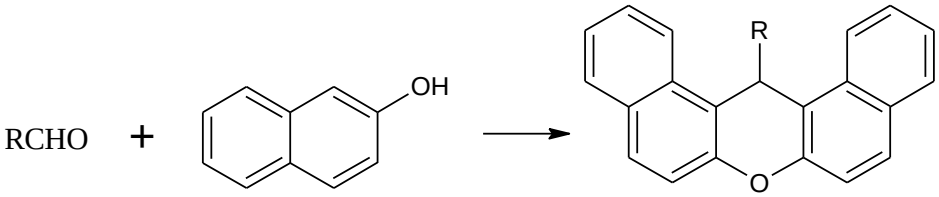
2. Synthesis Synthesis of 1- Amidoalkyl - 2-napthols.



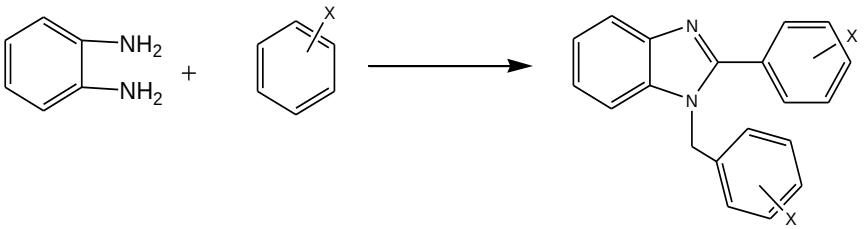
3. Synthesis of 1, 8-Dioxo-Octahydroxanthenes.



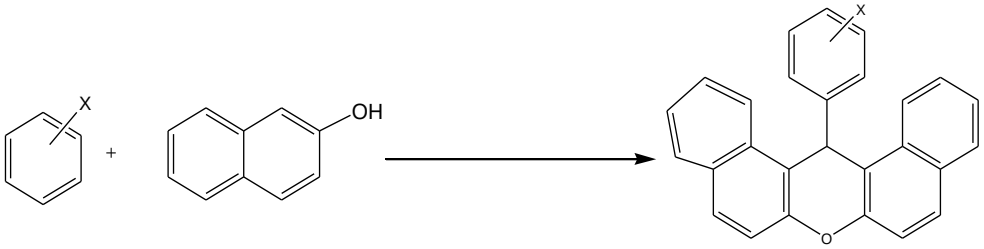
4. Synthesis of 14-aryl or alkyl-14-H-dibenzoxanthenes



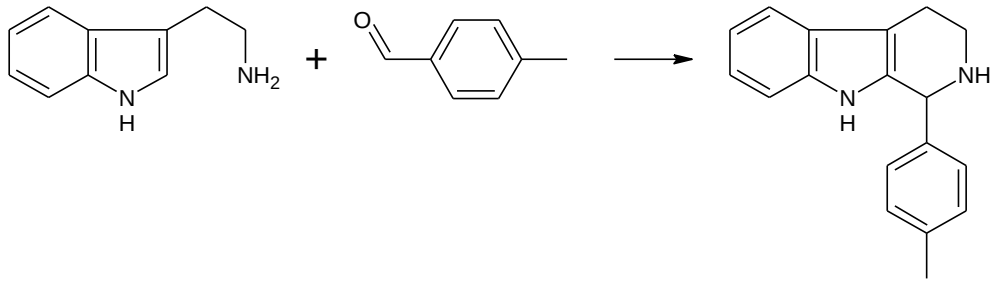
5. Synthesis of 2-Aryl Benzimidazoles.



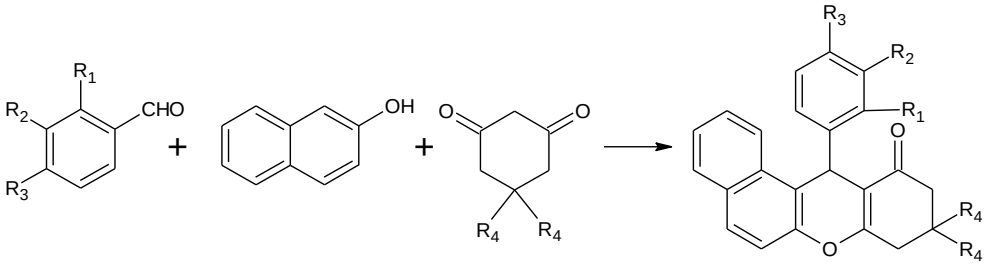
6. Synthesis of Aryl-14H-Dibenzoxanthene.



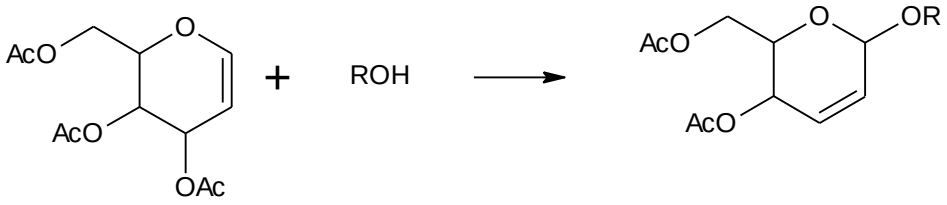
7. Pictet–Spengler reaction.



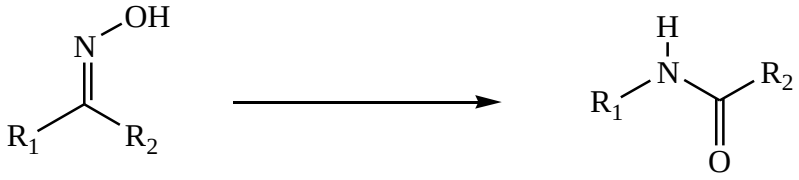
8. Synthesis of Xanthene and Benzoxanthene.



9. Synthesis of 2,3-unsaturated O-glycosides.

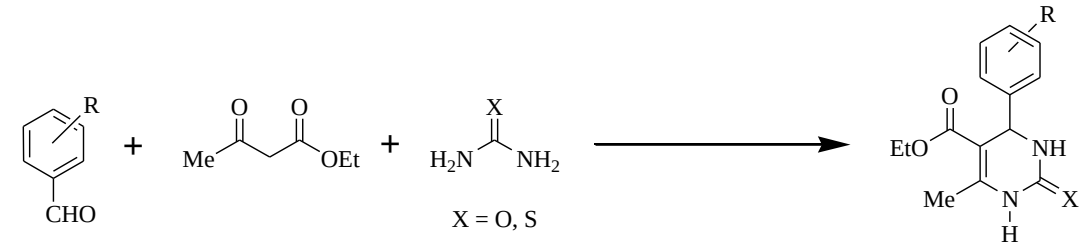


10. Beckmann Rearrangement reaction.



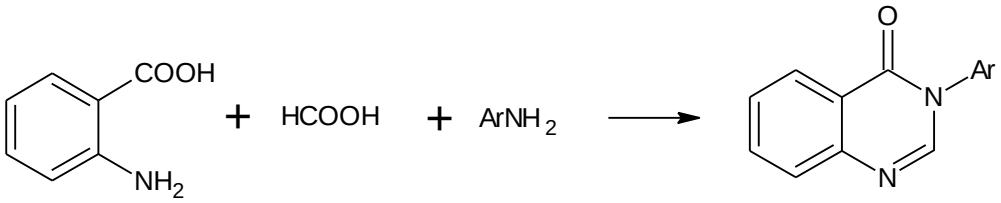
R_1, R_2 = Alkyl, Aryl

11. Biginelli reaction.



R = Cl, OH, NO_2, OMe, Me

12. Synthesis of quinazolin-4-(3H)-ones.



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